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# Sustainable bio-ethanol production from agro-residues: A review

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A B S T R A C T

Due to increasing population and industrialization, the demand of energy is increasing day by day. Simultaneously, the worldwide bio-ethanol production is increasing constantly. The maize, sugarcane and sugar beets are major traditional agricultural crops used as bio-ethanol production but these crops are unable to meet the global demand of bio-ethanol production due to their primary value of food and feed. Hence, cellulosic materials such as agro-residues are attractive feedstock for bio-ethanol production. The cellulosic material is the most abundant biomass and agro-residues on the earth. Bio-ethanol from agro-residues could be a promising technology that involves four processes of pre-treatment, enzymatic hydrolysis, fermentation and distillation. These processes have several challenges and limitations such as biomass transport and handling, and efficient pre-treatment process for removing the lignin from the lignocellulosic agro-residues. Proper pre-treatment process may increase the concentrations of fermentable sugars after enzymatic hydrolysis, thereby improving the efficiency of the whole process. Others, efficient microbes and genetically modified microbes may also enhance the enzymatic hydrolysis. Conversion of cellulose to ethanol requires some new pre-treatment, enzymatic and fermentation technologies, to make the whole process cost effective. In this review, we have discussed about current technologies for sustainable bioethanol production from agro-residues.



**Contents**



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## 1. Introduction

Due to increasing population, the demand of energy is increasing throughout the world. Currently, the primary source of energy is the fossil fuel and non-renewable sources such as natural gas, oil and coal. These have been used for the production of fuel, electricity and others goods [1]. It has been proposed that such resources would be depleted rapidly near future. The extreme consumption of fossil fuels, especially in large urban areas, has caused more pollution due to release of green house gases (GHGs) during the last few decades. The concentration of GHGs in the biosphere has hugely increased [2]. For subsistence of one's on the earth must require energy, is the most important part for human beings for their growth and development. And it has been deduced that about 13-fold energy consumption increased in 20th century, which is faster than that of increasing population [3–6]. The other interference concludes that about one-quarter of world's population do not access a fraction of energy [7]. We are consuming both renewable as well as non-renewable energies and due to the overconsumption and exploitation of non-renewable energy resources, eventually, all petroleum reserves will be completely depleted; therefore, people are approaching towards the use of renewable source of energy. Consequently, overconsumption of non-renewable energy sources scaling up the price of oil and exacerbating our environment. According to World Energy Council petroleum, natural gas and coal (non-renewable energy sources), which are the good source of energy, collectively contribute nearly 82% of global energy needs and one fifth of the $CO_2$ emission is due to 60% of petroleum based fossils fuel [8]. Hence to reduce the dependency on these resources a considerable promising shift is needed to utilize the alternative, sustainable as well as renewable sources of energy such as solar, wind, water, biomass and geothermal heat for the energy industry. The chemical industry may depend on biomass as an alternative source in the near future [6]. About 80% world's wind energy is produced by California in the form of Electricity and it has been accounted that Denmark, the world's second largest producer of wind energy, gained 2% of its power through wind turbine in 1990 [9]. Alternative sources of energy are being used in various countries. Biomass like cellulosic agricultural waste is the most abundant biomass on the earth. Using biomass like cellulosic agricultural waste is the potential promising natural renewable, inexpensive, cost effective and sustainable sources used for considerable and commercial production of bio-energy as bio-ethanol. The renewable fuels such as bio-diesel and bio-hydrogen, derived from sugarcane, corn, switchgrass, algae, etc., can be used as petroleum-based fuels in the future as fossil fuels are going to depleted soon due to higher energy consumption.

The limited amount of such alternative energy sources leading us looking for sustainable energy sources i.e., bio-energy. The concept of bio-energy came by dint of pervasive overexploitation of fossils fuel and alternative resources. Bio-energy is the renewable source of energy using natural resources for the production of sustainable bio-fuels. Bemdes et al. [10] estimated that the potential global bio-energy supply range from less than 100 to over 400 EJ/year for 2050 [11]. Biofuel includes solid, liquid and gas and the major biofuels encompass bio-ethanol, biodiesel, biogas, bio-methanol, bio-syngas ($CO+H_2$), bio-oil, bio-char, bio-hydrogen, Fischer–Tropsch liquids petroleum, and vegetable oil, out of which bio-ethanol and biodiesel are liquid transportation fuel, used as an additive source. Bio-ethanol is a gasoline alternate while biodiesel is a diesel alternate to reduce the GHGs emission when blended as an additive. Bio-ethanol produced about 60% from sugarcane and 40% from other crops, while biodiesel from inedible vegetable oil, waste oil and grease and it was estimated that in 2007 about 60 billion liters bio-fuels produced globally [12]. It has been accounted that bio-ethanol could sink about 90% $CO_2$ and 60–80% $SO_2$ when blend with 95% gasoline [13,14]. It has also been observed that bio-ethanol is being produced by various biomasses, which are naturally available on the earth. Biomass (bestows just about 14% of world's energy), is the fourth largest source of energy after petroleum, coal and natural gas [15].

Countries across the globe have well thought-out and directed state policies toward the improved and cost-effective utilization of biomass for summit their future energy demands in order to meet carbon dioxide decline targets as specified in the Kyoto Protocol as well as to reduce reliance and dependence on the supply of fossil fuels [16]. Since biomass can be used as a huge source for bio-ethanol production, it is generally used to produce both power and heat, usually during combustion. Recently, ethanol is broadly used as liquid bio-fuel for motor vehicles [17,18]. The significance of ethanol is higher due to various reasons such as global warming and climate change. Bio-ethanol production has been increasing widespread interest at the international, national and regional levels. The worldwide market for bio-ethanol production and demand has entered a phase of rapid, transitional growth. The focus toward renewable sources for power production in various countries of the world has been shifted due to depletion of crude oil reserves. Ethanol has prospective as an important substitute of gasoline in the transport fuel market. On the other hand, the cost of bio-ethanol production is higher as compared to fossil fuels.

The world bio-ethanol production in 2008 was 66.77 billion liters [19]. It has grown to 88.69 billion liters in 2013 and is expected to reach 90.38 billion liters in 2014 [20]. Brazil and the USA are the two major ethanol producing countries of 26.72% and 56.72%, respectively of the world production [19]. Huge scale production of ethanol bio-fuel is mainly depended on sucrose from sugarcane in Brazil or starch, mainly from corn, in USA. Presently, ethanol production depending up on corn, starch and sugar substances may not be popular due to their food and feed value. The price is a significant factor for large scale extension of bio-ethanol production. The green gold petroleum from lignocellulosic wastes avoids the existing struggle of food versus fuel caused by grain dependent bio-ethanol production [18]. Kim and Dale [21] reported that 442 billion liters of bio-ethanol can be produced from lignocellulosic biomass and that total crop residues and wasted crops can produce 491 billion liters of bio-ethanol per year, about 16 times higher than the actual world bio-ethanol production. The cellulosic materials are renewable, low cost and are available in large quantities. It includes crop residues, grasses, sawdust, wood chips, agro-waste etc. Many scientists and researchers have been working on ethanol production from lignocellulosics in the past two decades [16,22–28]. Hence, bioethanol production could be the route to the effective utilization of agricultural residue and wastes. Rice straw, wheat straw, corn straw, cotton seed hair, seaweed, paper, pineapple leaf, Banana stem, Jatropha waste, Poplar aspen; Oil palm frond and sugarcane bagasse are the major agro-residue in terms of quantity of biomass available [21]. For bioethenol production from the cellulosic material of agro-residues, three processes like pretreatment, enzyme hydrolysis and fermentation are required.

**Table 1**
Bio-ethanol production from different countries from year 2004 to 2014 [40].

| Country | 2004 | 2005 | 2006 | 2007 | 2008 | 2009 | 2010 | 2011 | 2012 | 2013 | 2014 |
|---|---|---|---|---|---|---|---|---|---|---|---|
| *Africa* | | | | | | | | | | | |
| Algeria | – | – | – | – | – | – | – | – | – | – | – |
| Egypt | – | – | – | – | – | – | – | – | – | – | – |
| Sub Saharan Africa | – | – | – | – | – | – | – | – | – | – | – |
| Republic of south Africa | 15.00 | 15.00 | 15.00 | 15.500 | 16.00 | 15.42 | 15.74 | 15.91 | 16.07 | 16.18 | 16.26 |
| *Latin America and Caribbean* | | | | | | | | | | | |
| Argentina | 174.00 | 157.00 | 205.00 | 225.00 | 315.0 | 416.26 | 440.61 | 454.73 | 468.93 | 483.22 | 497.60 |
| Brazil | 15,207.91 | 15,806.93 | 17,931.65 | 22,445.98 | 27,674.08 | 25,804.17 | 28,960.15 | 31,391.68 | 34,298.50 | 37,395.71 | 40,625.33 |
| Uruguay | – | – | – | – | – | – | – | – | – | – | – |
| *Asia* | | | | | | | | | | | |
| Bangladesh | – | – | – | – | – | – | – | – | – | – | – |
| China | 3673.00 | 3438.00 | 3509.00 | 3679.00 | 3964.00 | 4109.00 | 4368.09 | 4648.94 | 4823.56 | 4961.93 | 5121.19 |
| India | 1178.21 | 1120.49 | 1663.52 | 2081.91 | 2084.54 | 1680.31 | 1703.58 | 2429.56 | 2481.79 | 2532.37 | 2574.75 |
| Indonesia | 163.15 | 177.36 | 176.46 | 196.05 | 208.21 | 240.30 | 424.57 | 440.57 | 461.78 | 485.20 | 509.64 |
| Iran | – | – | – | – | – | – | – | – | – | – | – |
| Malaysia | 79.28 | 62.28 | 63.28 | 64.30 | 64.00 | 66.25 | 66.48 | 66.84 | 67.03 | 67.48 | 67.98 |
| Pakistan | – | – | – | – | – | – | – | – | – | – | – |
| Saudi Arabia | – | – | – | – | – | – | – | – | – | – | – |
| *Europe* | | | | | | | | | | | |
| EU-27 | 2576.00 | 2940.00 | 3701.00 | 3887.00 | 5021.00 | 5761.52 | 6465.07 | 7538.66 | 9154.72 | 10,795.30 | 11,773.80 |
| Russia | – | – | – | – | – | – | – | – | – | – | – |
| Ukraine | – | – | – | – | – | – | – | – | – | – | – |
| *OECD countries* | | | | | | | | | | | |
| Canada | 396.07 | 405.80 | 544.72 | 839.17 | 1083.40 | 1130.82 | 1572.55 | 1703.18 | 1713.60 | 1729.65 | 1721.32 |
| United State | 12,596.45 | 15,332.23 | 20,171.23 | 28,929.30 | 35,190.54 | 40,543.66 | 46,024.27 | 49,113.61 | 51,321.62 | 54,057.70 | 57,199.60 |
| Australia | – | 27.20 | 62.70 | 100.00 | 155.77 | 238.00 | 383.72 | 386.46 | 389.23 | 392.01 | 394.82 |
| New Zealand | – | – | – | – | – | – | – | – | – | – | – |
| Mexico | 35.00 | 58.00 | 49.00 | 61.00 | 61.00 | 65.69 | 70.38 | 75.08 | 76.95 | 78.83 | 80.71 |
| Korea | – | – | – | – | – | – | – | – | – | – | – |
| Japan | – | 113.00 | 113.00 | 110.09 | 110.20 | 100.20 | 100.20 | 130.00 | 130.00 | 130.00 | 130.00 |
| Turkey | 19.02 | 46.58 | 50.76 | 44.34 | 54.34 | 64.34 | 64.99 | 65.18 | 65.49 | 65.76 | 65.86 |
| Chile | – | – | – | – | – | – | – | – | – | – | – |
| *OECD* | 15,627.12 | 18,876.23 | 24,641.65 | 33,926.47 | 41,621.71 | 48,194.26 | 54,616.20 | 58,946.99 | 62,786.13 | 67,183.49 | 71,300.25 |
| *Non-OECD* | 21,048.01 | 21,449.19 | 24,562.10 | 29,880.07 | 35,560.43 | 33,942.15 | 37,964.09 | 41,750.49 | 45,199.78 | 48,806.26 | 52,544.86 |
| *Developed* | – | 18,818.23 | 24,592.65 | 33,865.56 | 41,560.91 | 47,774.20 | 54,545.82 | 58,871.91 | 62,709.17 | 67,104.66 | 71,219.54 |
| *Developing* | – | – | – | – | – | – | – | – | – | – | – |
| *Least developed countries* | – | – | – | – | – | – | – | – | – | – | – |

The pre-treatment is the most important and initial process for separation of free cellulose from agro-residues. Second process of enzyme hydrolysis is also important, which has been done by efficient microbes that have ability to secrete cellulose enzyme [29,30].This enzyme involves in hydrolysis of cellulose to glucose. Several microbial species of *Clostridium*, *Cellulomonas*, *Thermonospora*, *Bacillus*, *Bacteriodes*, *Ruminococcus*, *Erwinia*, *Acetovibrio*, *Microbispora*, *Streptomyces* are capable to produce cellulase enzyme. Many fungi such as *Trichoderma*, *Penicillium*, *Fusarium*, *Phanerochaete*, *Humicola*, *Schizophillum* sp. also have been reported for cellulase production [16,31,32]. After this, fermentation process is required for conversion of glucose to ethanol by microbes e.g. *Saccharomyces cerevisiae*, *Escherichia coli*, *Zymomonas mobilis*, *Pachysolen tannophilus*, *Candida shehatae*, *Pichia stipitis*, *Candida brassicae*, *Mucor indicus* etc. [28,33–37]. These processes are required for sustainable bioethenol production from cellulosic material of agro-residues. The main aim of this review is to present a brief overview of the available and accessible technologies for bioethanol production using major cellulosic materials of agro-residue. The use of agro-residues for the production of bioethanol is environment friendly and socially acceptable technology and also reduces the green house gas emission [38].

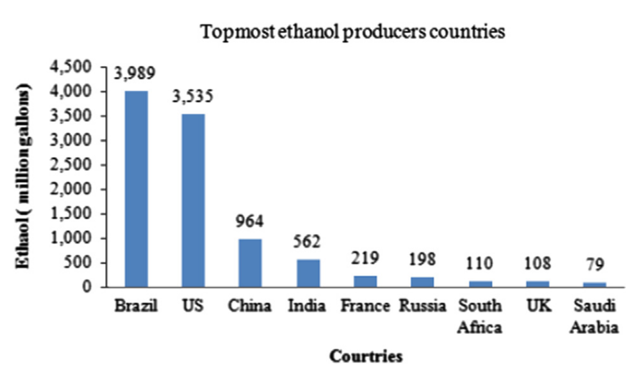


**Fig. 1.** Topmost ethanol producing countries [47].

## 2. Global standpoints of bio-ethanol production from cellulosic materials

### 2.1. International scenario

The 'first oil crisis' came during the post world war II in 1973 due to soaring demand of petroleum and scaling up burning of

transportation bio-fuel more [39]. The World Watch Institute estimated that the world's oil consumption increased from 2004–2005 and demand increased by 5.3%, typically in China, US, Canada and UK. US, independently was the world's biggest polluter in 2005 and consumed about 140 billion gallons of transportation fuel and more than 308 million metric tons of carbon emitted into the atmosphere by the gas-guzzling vehicles (2006). The OECD-FAO agriculture outlook has estimated the bio-ethanol production of different countries in Table 1 [123]. Antoni [62] calculated that globally about $48.7 \times 10^6$ $m^3$/ annum of bio-ethanol produced in 2005, of which 72.6% was produced in Brazil and USA. Reijnders and Huibregts [39] also estimated that some of promising countries are being produced bio-ethanol such as India, Russia, Southern Africa, Thailand and the Caribbean too [42–46] and they calculated that global bio-ethanol production by volume was about $51 \times 10^6$ $m^3$ in 2006 and in 2007 it was about $54 \times 10^6$ Mg [47,39]. Herrera [47] reported that the world topmost ethanol producer countries e.g. Brazil, US, China, India, France, Russia, South Africa, UK and Saudi Arabia as shown in Fig. 1 [47]. The total ethanol production in 2008 was about 7266.8 Millions of gallon and the largest ethanol producer country in 2008 is United States, which produced nearly 9000 Millions of

**Table 2**
World's total production of fuel ethanol (billion liters) from year 2004 to 2013 [56,73–75,77–82,196,197,198].
*Source*: adopted from [34].

| Countries | Major feedstock sugar and starchy crops | Ethanol production (billion liters) per year | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | 2004 | 2005 | 2006 | 2007 | 2008 | 2009 | 2010 | 2011 | 2012 | 2013 |
| US | Corn/maize | 13 | 15 | 18.3 | 24.6 | 34 | 41 | 49.5 | 54.2 | 50.4 | 50.3 |
| Brazil | Sugarcane | 15 | 15 | 17.5 | 19 | 27 | 26 | 27.6 | 21.0 | 21.6 | 25.5 |
| Germany | Wheat | 0.02 | 0.2 | 0.5 | – | 0.5 | 0.8 | 1.5 | 0.8 | 0.8 | 0.8 |
| France | Sugar beet, wheat | 0.1 | 0.15 | – | – | 1.2 | 0.9 | 1.1 | 1.1 | 1.0 | 1.0 |
| China | Corn, sugarcane, maize, cassava | 2 | 1 | 1 | 1.8 | 1.9 | 2.1 | 2.1 | 2.1 | 2.1 | 2.0 |
| Argentina | Sugarcane | – | – | – | 0.02 | – | – | 0.1 | 0.2 | 0.2 | 0.5 |
| Italy | Cereals | – | – | 0.13 | – | 0.13 | 0.1 | 0.1 | 0.0 | – | – |
| Spain | Barley, wheat | 0.2 | 0.3 | 0.4 | – | 0.4 | 0.4 | 0.6 | 0.5 | 0.4 | 0.4 |
| India | Sugarcane, wheat | – | 0.3 | 0.3 | 0.2 | 0.3 | 0.2 | – | – | 0.5 | – |
| Canada | wheat/cereal | 0.2 | 0.2 | 0.2 | 0.8 | 0.9 | 1.1 | 1.4 | 1.8 | 1.8 | 1.8 |
| Poland | Rye | – | 0.05 | 0.12 | – | 0.12 | – | 0.2 | – | – | 0.2 |
| Czech Republic | Sugar beet | – | 0.15 | 0.0 | – | – | – | – | – | – | – |
| Colombia | Sugarcane | – | 0.2 | 0.2 | 0.3 | 0.3 | 0.3 | 0.4 | 0.3 | 0.4 | 0.4 |
| Sweden | Wheat | – | 0.2 | 0.14 | – | 0.14 | – | – | – | – | – |
| Malaysia | – | – | – | – | – | – | – | – | – | – | – |
| UK | – | – | – | – | – | – | 0.2 | 0.3 | – | – | – |
| Denmark | Wheat | – | 0.1 | – | – | – | – | – | – | – | – |
| Austria | Wheat | – | 0.1 | – | – | – | 0.1 | – | – | 0.2 | – |
| Slovakia | Corn | – | 0.1 | – | – | – | – | – | – | | – |
| Thailand | Sugarcane, cassava | 0.2 | – | – | 0.3 | 0.3 | 0.4 | 0.4 | 0.5 | 0.7 | 1.0 |
| Australia | Sugarcane | 0.07 | – | – | 0.1 | – | – | – | | | 0.3 |
| Belgium | wheat | – | – | – | – | – | 0.2 | 0.3 | 0.4 | 0.4 | 0.4 |
| EU | Various/cereal and suga rbeet | – | – | – | 2.16 | – | – | 4.5 | 4.3 | 4.2 | 4.5 |
| World total | | 31 | 33 | 39 | 49.6 | 67 | 76 | 86 | 86.1 | 83.1 | 87.2 |

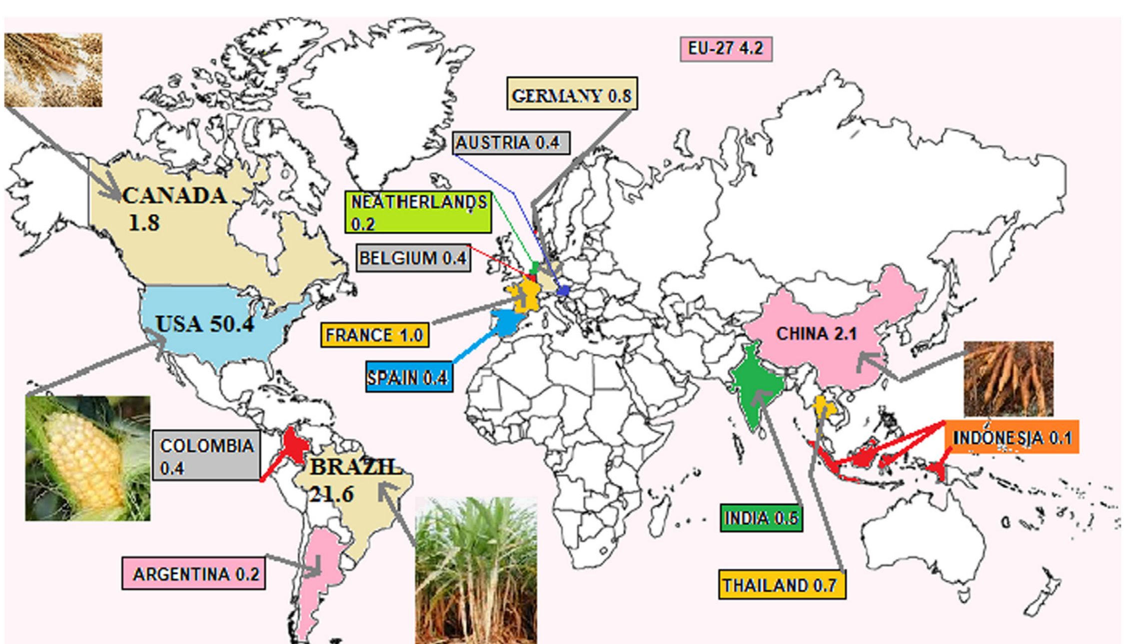


**Fig. 2.** Ethanol production (billion liters) in 2012 [48–51].

**Table 3**
Annual estimate of world crop yield/world crop residue production in 2010 ($10^4$ ton) [57,58].

| Crops | Africa | | America | | Asia | | Europe | | Oceanic | | World | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Grains | Yield/residue | | Yield/residue | | Yield/residue | | Yield/residue | | Yield/residue | | Yield/residue | |
| Barley | 668 | 1004 | 1603 | 2409 | 1975 | 2969 | 7349 | 11,050 | 760 | 1143 | 12,345 | 18,576 |
| Maize | 6358 | 6358 | 44,534 | 44,534 | 24,575 | 24,575 | 8510 | 8510 | 53 | 53 | 84,031 | 84,031 |
| Millet | 1527 | 2316 | 27 | 41 | 1567 | 2378 | 33 | 50 | 4 | 6 | 3158 | 4792 |
| Oats | 20 | 20 | 508 | 508 | 98 | 98 | 1195 | 1195 | 142 | 142 | 1962 | 1962 |
| Rice | 2298 | 3449 | 3697 | 5549 | 63,184 | 94,830 | 432 | 649 | 21 | 31 | 69,632 | 104,507 |
| Rye | 7 | 10 | 248 | 377 | 167 | 254 | 2267 | 3450 | 54 | 81 | 2572 | 3914 |
| Sorghum | 2111 | 3166 | 2251 | 3376 | 980 | 1469 | 71 | 106 | 160 | 240 | 5572 | 8358 |
| Wheat | 2210 | 3318 | 11,273 | 16,919 | 29,252 | 43,904 | 20,371 | 30,575 | 2258 | 3389 | 65,365 | 98,104 |
| Total | 15,198 | 19,640 | 64,141 | 73,715 | 121,798 | 170,477 | 40,229 | 55,585 | 3452 | 5086 | 244.648 | 32,4244 |
| *Sugar crops* | | | | | | | | | | | | |
| Sugar beet | 1028 | 259 | 3103 | 782 | 3663 | 924 | 15,051 | 3795 | 0 | 0 | 22,845 | 5760 |
| Sugar cane | 8959 | 2242 | 96,384 | 24,115 | 62,410 | 15,615 | 1 | 0 | 3355 | 839 | 171,109 | 42,811 |
| Total | 9987 | 2501 | 99,487 | 24,898 | 66,073 | 16,538 | 15,052 | 3795 | 3355 | 839 | 193,954 | 48,571 |
| *Tubers* | | | | | | | | | | | | |
| Potatoes | 2233 | 558 | 3966 | 991 | 15,250 | 3812 | 10,812 | 2703 | 181 | 45 | 32,442 | 8111 |
| Sweet potato | 1522 | 383 | 0 | 0 | 94 | 24 | 5 | 1 | 74 | 19 | 10,764 | 2711 |
| Total | 3755 | 942 | 3966 | 991 | 15,344 | 3836 | 10,817 | 2704 | 255 | 64 | 43,206 | 10,821 |

**Table 4**
Potential bio-ethanol production (GL) from food crop by continent [21].

| Continents | Corn | Barley | Oat | Rice | Wheat | Sorghum | Sugarcane | Total |
|---|---|---|---|---|---|---|---|---|
| Africa | 2.17 | 0.12 | 0.002 | 0.71 | 0.55 | 1.55 | 0.23 | 5.33 |
| Asia | 6.82 | 0.83 | 0.04 | 14.4 | 6.78 | 0.37 | 0.82 | 30.1 |
| Europe | 1.09 | 1.35 | 0.30 | 0.02 | 2.70 | 0.003 | – | 5.45 |
| North America | 0.21 | 0.005 | 0.01 | 0.63 | 0.02 | – | – | 0.87 |
| Central America | 1.21 | 0.01 | 0.0004 | 0.05 | 0.16 | 0.09 | 0.18 | 1.70 |
| Oceania | 0.01 | 0.13 | 0.001 | 0.02 | 0.54 | 0.0004 | 0.0001 | 0.70 |
| South America | 2.87 | 0.03 | 0.03 | 0.93 | 0.60 | 0.12 | 0.37 | 4.95 |

gallon and the least ethanol producer country in 2008 is Paraguay, which produced nearly 23.7 Millions of gallon [52]. It has been found that US (by corn) is the first and Brazil (by sugarcane), is the second largest producer of bio-ethanol followed by China in the world [53]. Cascone [42] reported that China produced bio-ethanol using sugarcane, cassava and yams, while the European Union by wheat and sugar beet [54,39]. In US, the cereals grains (including wheat and maize) are also used for ethanol production [55]. Timilsina and Shreshtha [56] reported bio-fuel production of different countries (about 23 countries) by using different crops by the year (2004–2009) and it was seen that many countries use sugar and starchy crops for bio-ethanol production, where these crops impose problem of food insecurity (Table 2). The worldwide bio-ethanol production is in billion liters during 2012 (Fig. 2) [48–51]. Wang [57] reported the annual crop yield and crop residue in 2010 and stated that quantity of grain and tubers produces much more higher residue than that of crop yield; simultaneously, the sugar crops produces lesser residue than yield (Table 3). It has also been estimated that about 75% biomass resources of total agriculture residues obtained from three major food crops viz., rice, wheat and maize [58,59]. Consequently, the bio-ethanol from food crops like corn, barley, wheat, oat, rice, sorghum and sugarcane produces somewhat lesser production than that of ligno-cellulosic non-food crops such as corn stover, barley straw, wheat straw, rice straw, Sorghum straw and Bagasse in Tables 4 and 5 [21]. In addition, various agro-wastes also indicate the higher production of bio-ethanol (Table 6) [21,60,61]. Despite these individual crops for energy production, emphasis is also given to use ago-residues such as lignocellulosic biomasses. It has deduced that the production from these ago-residues provide higher bio-ethanol production, which could diminish the predicament of world's food crisis. The bio-ethanol yield from rice, maize and wheat is lower than that of energy crops like Miscanthus, Sweet sorghum and Switchgrass (Table 7) [58]. Simultaneously, the production cost was also estimated, indicating that the bio-waste or lignocellulosic agro-waste imposes lesser cost (0.14–0.43 US$/L only for production) than other crops (Table 8) [52,63-70,122]. In totality the problem of food security as well as food crisis could be overcome by using lignocellulosic materials for ethanol production for ever growing escalation populace.

According to OECD/ITF [71], the support from US Government for the production of bio-fuels has been motivated primarily by agricultural and energy policies with the aim of substituting bio-fuels for imported oil and supporting farm incomes and agricultural sector industries. More recently, support for bio-fuels has become a core part of many national policies for reducing transport sector $CO_2$ emissions. Subsidies for bio-fuels are growing rapidly and are estimated to have reached around USD 15 billion in 2007 for the OECD as a whole. The European Union requires Member States to take measures to ensure that bio-fuels account for 2% of the demand for transport fuels, rising to 5.75% in 2010. The European Commission proposes increasing the target to 10% by 2020. The US Government set a target of 4 billion gallons of ethanol for 2006, nearly 3% of the gasoline market, and has proposed a target of 35 billion gallons of bio-fuels production by 2017, which is expected to account for about 9% of transport sector fuel consumption. However, all bio-fuels are not equally effective in substituting for oil or in cutting greenhouse gas emissions and promoting their production can have unintended consequences. Subsidies for bio-fuels, and the resultant increase in demand for grain and oil seeds, appears to have contributed to sharp increases in food and livestock feed prices in world markets, in a context of rising demand for these commodities for traditional uses. Also, depending on feedstock and farming practices, bio-fuels production can have significant environmental costs. These include degradation of biodiversity and soil fertility and increased rates of soil erosion, excessive water abstraction and water pollution. In some circumstances, bio-fuel feedstock production can even result in a net increase in GHG emissions. The US is the world's largest producer of ethanol, making some 13–14 billion gallons of renewable fuel annually. In 2005, the US Congress passed the Energy

**Table 5**
Potential bio-ethanol production (GL) from lignocellulosic (non-food) biomass by continent [21].

| Continents | Corn stover | Barley straw | Oat straw | Rice straw | Wheat straw | Sorghum straw | Bagasse | Total |
|---|---|---|---|---|---|---|---|---|
| Africa | – | – | – | 5.86 | 1.57 | – | 3.33 | 10.8 |
| Asia | 9.57 | 0.61 | 0.07 | 186.8 | 42.6 | – | 21.3 | 261.0 |
| Europe | 8.23 | 13.7 | 1.79 | 1.10 | 38.9 | 0.10 | 0.004 | 63.8 |
| North America | 38.4 | 3.06 | 0.73 | 3.06 | 14.7 | 1.89 | 1.31 | 63.2 |
| Central America | – | 0.05 | 0.009 | 0.77 | 0.82 | 0.31 | 5.46 | 7.42 |
| Oceania | 0.07 | 0.60 | 0.12 | 0.47 | 2.51 | 0.09 | 1.84 | 5.70 |
| South America | 2.07 | 0.09 | 0.06 | 6.58 | 2.87 | 0.41 | 18.1 | 30.2 |

**Table 6**
Potential bio-ethanol production (GL) from agro-waste by continent. Adopted from [21,60,61].

| Continents | Wheat wastes (Tg)/total bioethanol (GL) | Sugar cane wastes/total bioethanol (GL) | Rice wastes/ total bioethanol (GL) | Barley wastes/ total bioethanol (GL) | Corn wastes/ total bioethanol (GL) |
|---|---|---|---|---|---|
| Iran | 7.5/3 | 4.3/0.63 | 1.05/0.378 | 0.6/0.21 | 0.5/0.2 |
| Asia | 16/50 | 77/23 | 690/202 | 3.5/2 | 45/20 |
| Africa | 7/3 | 13/4 | 22/7 | 0.5/0.5 | 3.5/2.5 |
| Europe | 140/42 | 0.01/0.004 | 4/2 | 47/15.5 | 31/10 |
| America | 65/20 | 90/26 | 40/12 | 11/3.5 | 150/45 |
| America | 10/4 | 7/2 | 2/0.5 | 2.5/1 | 0.5/0.1 |
| World | 382/119 | 187.01/55.004 | 758/223.5 | 64.5/22.5 | 230/22.5 |

**Table 7**
Biomass and bio-ethanol yield of different species [58].

| Species | Photosynthetic type | Biomass yield (tons/ ha/yr) | Bioethanol Yield (tons/ ha/yr) |
|---|---|---|---|
| Switchgrass | $C_4$ | 14–20 | 4–5 |
| Miscanthus | $C_4$ | 60–80 | 6–8 |
| Rice | $C_3$ | 15–30 | 1.5 |
| Wheat | $C_3$ | 15–30 | 1.5 |
| Maize | $C_4$ | 15–45 | 1.5 |
| Sweet sorghum | $C_4$ | 60–80 | 4–6 |

Policy Act, and in 2007, the Energy Independence and Security Act (EISA) creating a Renewable Fuels Standard (RFS) that required a minimum volume of renewable fuel to be blended into US petroleum fuel in increasing amount each year until 2022. The EISA renewable fuels standard (known as RFS2), established a target of 36 billion gallons of renewable fuels in US gasoline by 2022. Nested within those 36 billion gallons are 16 billion gallons of cellulosic ethanol (CE). According to EISA (2007) established life cycle greenhouse gas (GHG) emissions thresholds for each category, requiring a percentage improvement is related to a baseline of the gasoline and diesel they replace. The conventional biofuels were produced from starch feedstock (corn, sorghum, wheat) in plants built after 2007 must demonstrate a 20% reduction in life cycle GHG emissions as compared to the baseline petroleum fuel. Biomass based diesel requires to reduce 50% in life cycle GHG emissions as compared to the baseline petroleum fuel, while the cellulosic bio-fuel derived from renewable feedstock containing cellulose, hemicellulose, or lignin. It must have life cycle GHG emissions at least 60% lower than the baseline petroleum fuel.

### 2.2. National scenario

The economy of developing country like India is being increased at a rate about 9% recently. During 2007, India consumed about 156 million tons of crude oil of which 77% was imported and it was also projected that its importation will raise about 6 million barrels per day by 2030, showing that now India approaching towards the grieve dependency of oil security [Ministry of Petroleum and Natural Gas, 2007], will formulate India as the third largest importer of oil (IEA, 2007) [202]. India produces 1.3 billion liters of ethanol from cane molasses against an installed capacity of 3.2 billion liters currently. India is adopting a new policy for ethanol production from cellulosic biomaterials, which is an E20 by 2017 and targets to produce more than 4 billion gallons per year by 2017 [72]. Timilsina and Shrestha [56] reported that bio-fuel production in India using Sugarcane and wheat are the major feedstock (Fig. 3) [56,73–83,84].

In India, about 121 GJ fuel/ ha bio-ethanol produced annually by means of sugarcane in Fig. 4 [86–90,200]. Sukumaran et al. [35] estimated that about 199.1 million metric tons (MMT) of sugarcane cultivated in excess of a huge area in India, therefore as consequence of millions metric tons of production of sugarcane generates surplus amount of harvested residue such as sugarcane tops (SCT) (i.e., leaves including top portion of plant, which is cut away) and about 74.9 (MMT) of SCT are available in India [91,92,93]. India is one of the major waste generator of coffee pulp, by using coffee and cashew apple pulp as a cellulosic biomass as a waste (agricultural residue) that also produce bio-ethanol; however, it was also reported that cashew apple pulp (CAP) and wet coffee pulp (WCP) contained lower lignin and higher cellulose [35]. Bhatia and Paliwa [94] stated that ethanol can also be produced by an agro-waste i.e., banana peels, which is rich in carbohydrates, crude protein and reducing sugars and owing to affordable and renewable low cost material makes it potential feedstock for ethanol production [53]. It has been also reported that like banana peels, the peels of Pineapple and Plantain, an empty fruit bunches [95], and other fruit wastes are also used for bio-ethanol production. These fruit wastes are Quince pomace, Macaúba (*Acrocomia aculeata*), Apple pomace and rotten banana), Stalks and tubers, Date palm, Fruit bunches and Palm oil empty fruit bunches (OPEFB) for bio-ethanol production (Tables 9 and 10) [96–101,102].

## 3. Cellulosic material as agro-residues for bioethanol production

Globally many agro-residues have been used to produce bioethanol such as rice-straw, wheat straw, sugarcane bagasse, sugarcane tops, cotton stalk, soft bamboo, bamboo processing wastes and all are considered as abundantly available feed stocks [91,103]. These agro-residues are also utilized as animal fodder, as domestic fuel. The consumption fraction of wheat straw, rice straw and corn straw is too low and varies according to geographical region [21]. Every year huge portion of agricultural residues is

**Table 8**
The cost of production of bio-ethanol in different country [52,63–70,122].

| Country | Raw material | Costs (US$/L) |
|---|---|---|
| Petrol (gasoline) | | 0.34 |
| Brazil | Sugarcane | 0.16–0.22 |
| India | Sugarcane | 0 |
| India | Sorghum | 0 |
| France | Sugar beet | 0.60–0.68 |
| Europe | Sugar beet | 0.45 |
| EU | Wheat | 0.36–0.57 |
| EU | sugarbeet | 0.43–0.73 |
| New Zealand | Whey | 0.42–0.49 |
| Canada | Corn | 0 |
| Canada | Wheat | 0 |
| Europe | Wheat | 0.42 |
| United States | Mix of lignocellulosic materials | 0.43 |
| Thailand | Cassava | 0.18 |
| China | Wheat | 0 |
| China | Corn | 0 |
| China | Molasses | 0.32 |
| China | Sweet sorghum | 0.29 |
| United States | Corn | 0.25–0.40 |
| US | Corn | 0.57 |
| | Corn stover | 0.61–0.78 |
| US | Corn fiber | 0.55 |
| US | Wheat straw | 0.59 |
| | Spruce (softwood) | 0.59–0.85 |
| | Salix (hardwood) | 0.65–0.96 |
| | Lignocellulose (biowaste) | 0.14–0.43 |

disposed as waste. Approximately 600–900 million tons per year rice straw is produced globally [104]. The dumping of rice straw is limited by the bulky of material, slow degradation in the soil, harboring of rice stem diseases, and high mineral content. While, only a small portion of globally produced rice straw is used as animal feed, the rest is removed from the field by burning, a common practice all over the world, increasing air pollution and affecting human health [105–108]. Open field burning of rice and wheat straw is already banned in many countries in Western. Europe and some other countries like India have considered it seriously. The 90% of corn straw in United States is left in the fields as agro-residues [109]. While, only 1% of corn straw is collected for industrial processing and about 5% is used as animal feed and bedding. The worldwide, bio-ethanol production from rice straw, wheat straw, corn straw and sugarcane bagasse is now a matter of interest [16].

The percentage distributions of cellulose, hemicelluloses and lignin on dry weight basis of various agro-residues have been depicted in Table 11 [16,84,93,110–119,199]. India, a tropical country is using conventional feed stocks viz., sugarcane, oil palm and maize for bio-fuel production [92]. Graiham-rowe [120] believed some energy crops such as willow or poplar tress can be grown on polluted soil and hence reduce the soil contamination. A perennial grass namely elephant grass (*Miscanthus* × *giganteus)* is photosynthetic royalty [121], is an alternative energy crop being grown to produce ethanol [85] and Switchgrass (*Panicum virgatum*) [38] are considered as a better candidates for the bio-ethanol production (Table 6) [21,60,61].

Demirbas [12] stated that the Second and third generation biofuels are also called advanced biofuels. During first generation of bio-fuel Sugar, starch, vegetable oils, or animal fats feedstocks were being used to produce biofuel such as bio-ethanol, biodiesel and biogas, second generation used non-food crops, wheat straw, corn, wood, solid waste, energy crop (Fig. 5a and b) [123–126], while third generation biofuels are produced by using algae that attract attention of researcher and scientist for bio-energy production; however, the main problem associated with algae is to culture in ponds because it makes merely 0.1% of the mass and rest of 99.9% water [126]. The fourth generation involves using vegetable oil for bio-fuel production [12,127].

Menon and Rao [128], Bisaria and Ghose [129] calculated that about $1.5 \times 10^{11}$ ton global yield of lignocellulosic biomass is derived typically from agricultural wastes once a year [130]. The plant cell wall of lignocellulosic agro-waste consist of Cellulose, hemicelluloses and lignin of which cellulose 40–50%, a linear syndiotactic (alternating spatial arrangement of the side chains) and unbranched and insoluble polymer of glucose connected together by β-l,4 glycosidic bonds, hemicellulose 25–30%, a branched heteropolymer of D-xylose, L-arabinose, D-mannose, D-glucose, D-galactose and D-glucuronic acid and lignin 15–20% composed of three major phenolic components, namely p-coumaryl alcohol, coniferyl alcohol and sinapyl alcohol and other extractable components in Fig. 6 [41,131,132]. There are various sources of cellulosic biomasses obtained by different feedstock and residues namely as given in Fig. 7 [133]. Many sources have been well-known for ethanol production but among these the cellulosic biomass, which is a sustainable liquid transportation fuel includes a wide range of plant materials, used to convert plant materials into valuable bio-energy on commercial lager scale at low cost [134].

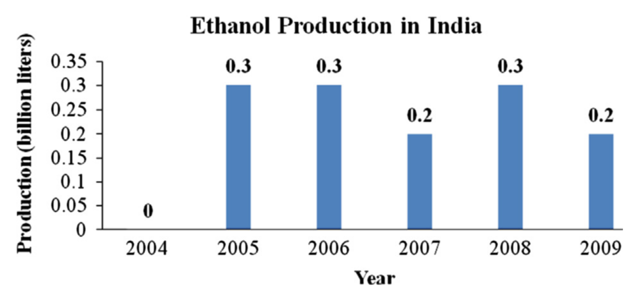


**Fig. 3.** Ethanol production in India using sugarcane and wheat [56,73–84].

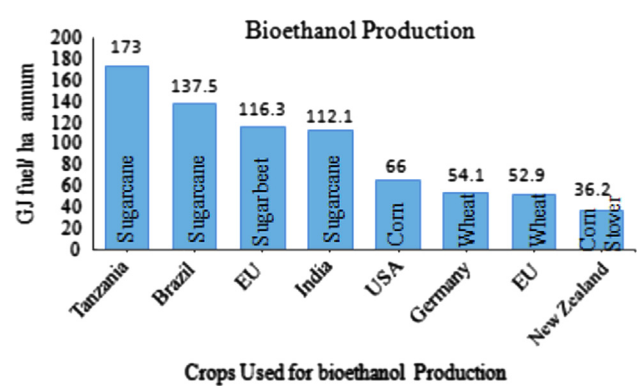


**Fig. 4.** Biofuel production of some countries and their yields in per hectare of year 2007 [85–90,200].

**Table 9**
Ethanol production from fruit waste.

| Fruit waste | Ethanol yield % | References |
|---|---|---|
| Pineapple peel | 8.34% (v/v) | [96] |
| Banana peel | 7.45% (v/v) | [98] |
| Plantain peel | 3.98% (v/v) | [98] |
| Apple pomace and rotten banana) | 38% | [99] |
| Palm oil empty fruit bunches (OPEFB) | 14.5% | [102] |

## 4. Pretreatment process

Pretreatment is necessary process to unwind cellulose from hemicelluloses and lignin in which cellulose is embedded [55] and make cellulose more susceptible for enzymatic hydrolysis [133]. It is most important and challenging process for the production of biofuel from the agroresudues. Lignocellulosic biomass is composed of three main constituents namely hemicellulose, lignin and cellulose. Pre-treatment methods refer to the solubilization and separation of one or more of these components of biomass. Such components are also treated by chemical or biological treatment, which give only cellulose [135]. The lignocellulosic complex is made up of a matrix of cellulose and lignin bound by hemicelluloses chains. Under pre-treatment process, the ligno-cellulosic matrix breaks down to reduce the degree of crystallinity of the cellulose and increase the part of amorphous cellulose. This form of cellulose is the most suitable form for enzymatic attack [34]. This process makes the lignocellulosic biomass susceptible to quick hydrolysis with increased yields of monomeric sugars [136]. The main aims of an effective pretreatment process are as follows: (i) formation of sugars directly or subsequently by hydrolysis, (ii) to avoid loss and/ or degradation of sugars formed, (iii) to limit formation of inhibitory products, (iv) to reduce energy demands and (v) to minimize costs. Physical, chemical and biological treatments are three types of pre-treatment process used. Thus pretreatment is imperative step to make cellulose susceptible for enzymatic hydrolysis. There are some characteristic features of pretreatment, which is efficient and effective for bio-ethanol production (Fig. 9) [13,14,128,133].

### 4.1. Physical pretreatment

The primary steps for ethanol production from agro-residues are combination of methods like milling, grinding or chipping. These methods reduce the cellulose crystallinity [31] and improve the efficiency of downstream processing. Wet milling, dry milling, vibratory ball milling and compression milling are usually done. The power applied for mechanical comminution of agricultural materials depends on the initial and final particle sizes, moisture content and on the nature of waste (hardwood, softwood, fibrous, etc.) being handled [27,31]. Smith et al. [137] and Weil et al. [138] stated some other physical methods of pretreatment like, compression milling, ball milling, cryomilling or attrition milling and steam treatment using poplar, wheat straw, newspaper, oat straw etc. Several physical technologies have been developed to disrupt the non-cellulosic component (i.e., lignin) to render cellulose and hemicelluloses so that it is more accessible for enzymatic hydrolysis [139,140]. Similarly, Kumar et al. [141] stated lignin that is composed of 10–15% of plant biomass contains no sugar and

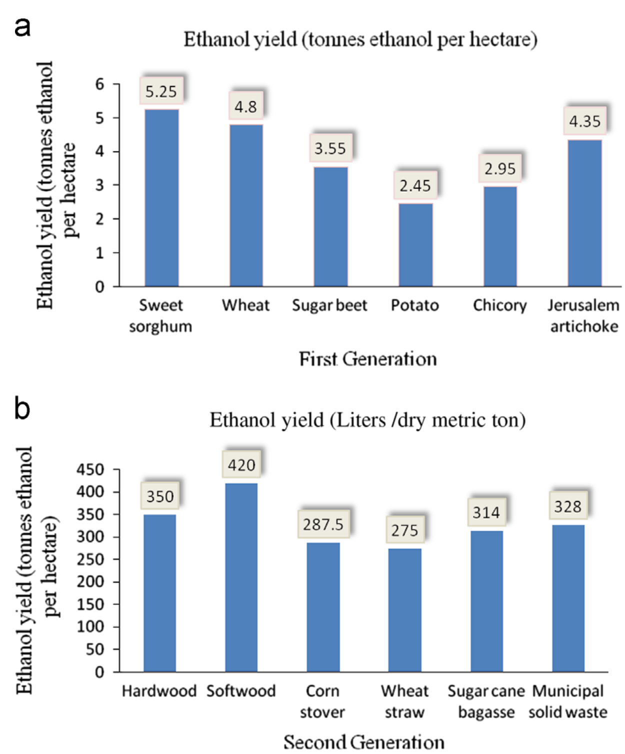


**Fig. 5.** (a) First and second generation bio-ethanol production of different bio-materials [122-126]. (b) Second generation bio-ethanol production of different bio-materials [122-126].

**Table 10**
Ethanol production from fruit waste.

| Fruit waste | Ethanol concentration (g/l) | References |
|---|---|---|
| Quince pomace | 19.66 | [97] |
| Macaúba (*Acrocomia aculeata*) | 5 | [98] |
| Stalks and tubers | 45.3 | [100] |
| Date palm | 136.00 ± 0.66 | [101] |

**Table 11**
Varying compositions of cellulose in different sources.

| Sources | Cellulose % | Hemicelluloses % | Lignin % | References |
|---|---|---|---|---|
| Corn stover | 31.0 (mf wt%) | 43.0 (mf wt%) | 13.0 (mf wt%) | [110,199] |
| Wheat straw | 32.4 (mf wt%) | 41.8 (mf wt%) | 16.7 (mf wt%) | [93,157] |
| Cereal straws | 35–40% | 26% | 15–20% | [93,111] |
| Poplar aspen | 42.3 (mf wt%) | 31.0 (mf wt%) | 16.2 (mf wt%) | [84,110] |
| Rice straw | 32.6 | 27.3 | 18.4 | [112] |
| Baggase | 65 (total carbohydrate) | | 18.4 | [16,113,114] |
| Seaweed (Sargassum spp.) | 20.35 (α) | 25.73 | – | [115] |
| Paper | 85–99 | 0 | 0–15 | [116] |
| Cotton seed hairs | 80–85 | 5–20 | 0 | [116] |
| Oil palm frond | 49.8 (α) | 83.5 (holocellulose) | 20.5 | [117] |
| Coconut | 44.2 (α) | 56.3 (holocellulose) | 32.8 | [117] |
| Pineapple leaf | 73.4 (α) | 80.5 (holocellulose) | 10.5 | [117] |
| Banana stem | 63.9 (α) | 65.2 (holocellulose) | 18.6 | [117] |
| Softwood | 40–50 | 25–30 | 25–35 | [201] |
| Hardwood | 40–50 | 25–35 | 20–25 | [193] |
| Big blustem (whole plant) | 29–37 | 21–25 | 17–24 | [118] |
| Switchgrass (whole plant) | 31–35 | 24–28 | 17–23 | [118] |
| Jatropha waste | 56.31 | 17.47 | 23.91 | [119,200] |

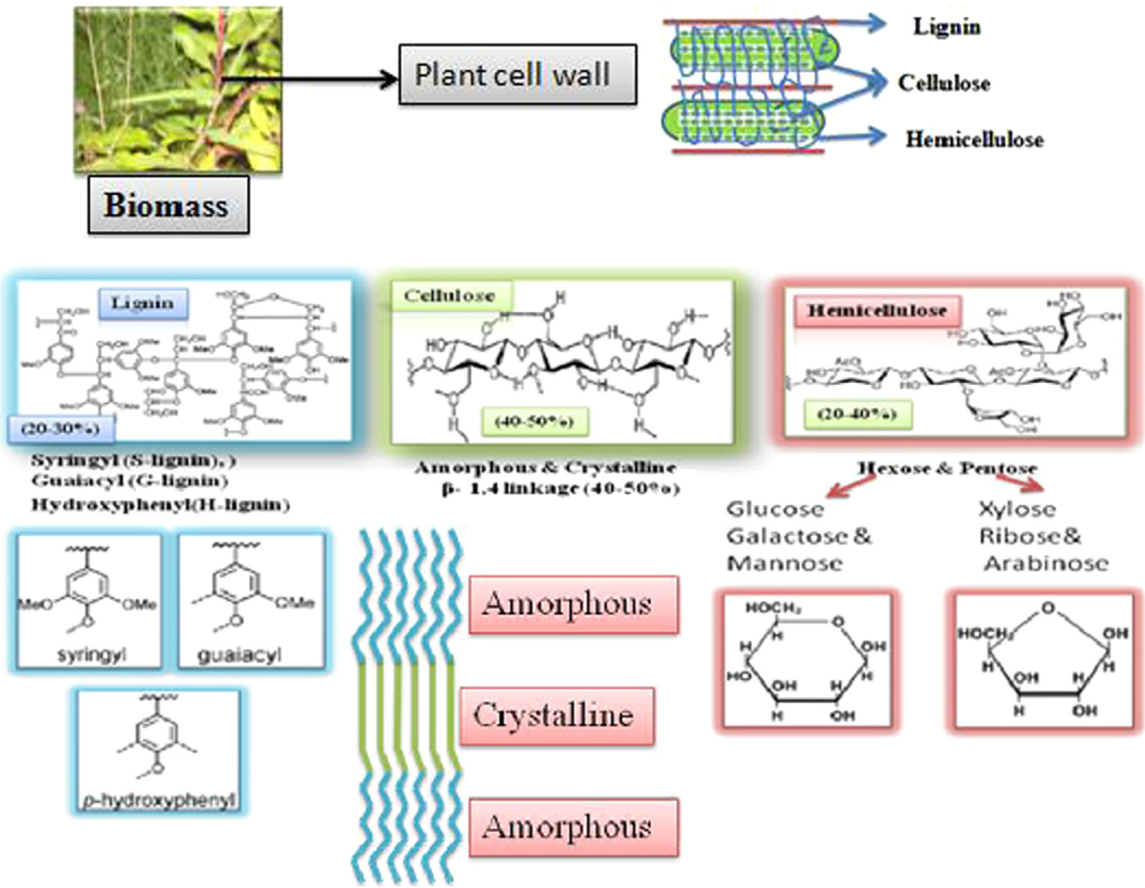


**Fig. 6.** Plant cell wall composition and its structure [41,131,132].

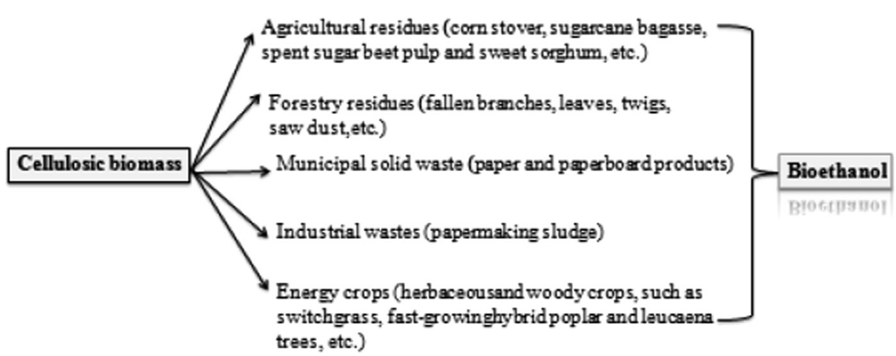


**Fig. 7.** Sources of cellulosic biomass [133].

throughout bio-processing it is left as a residue therefore; it is immense challenge for scientist and researcher to switch it into value added product [141]. Basically physical process is used to diminish the particle size and to increase the surface area for enzymatic attack [141] and digestibility of crystalline form of cellulose by improving mass transfer characteristics from reduction in particle size. The physical pretreatment technology includes uncatalyzed steam-explosion, liquid hot water (LHW) pretreatment, mechanical comminution and high energy radiation (Fig. 8) [142] of which steam explosion loosen the recalcitrant structure of plant cell wall by increasing surface area and removes pentose sugar but the major drawback of steam treatment during enzymatic hydrolysis it generates some cellulase inhibitory compounds and this inhibitory compound hampers the enzymatic hydrolysis of the cellulose substrates [141]. The physical process requires more energy inputs; at some stage in fermentation process it releases some inhibitory compounds which are more expensive [140]. Hence for commercial production, the physical process is quite expensive and probably could not be used as full-scale process.

### 4.2. *Chemical pretreatment*

Various chemical technologies are being used by Zheng et al. [142] and some other chemical pretreatments have been described by Kumar et al. [141] that are generally practiced include sodium hydroxide, perchloric acid, peracetic acid, acid hydrolysis using sulfuric and formic acids, ammonia freeze explosion, and organic solvent e.g. *n*-propylamine, ethylenediamine, *n*-butylamine etc. [138,143]. But the major impedance of chemical pretreatment the utilization of such chemicals affects the total economy of bioconversion of cellulosic biomass. The chemical pretreatment have

formerly and comprehensively been used in paper industry for lignin demolition in cellulosic materials to produce high quality paper products [128]. Shenoy et al. [93] showed that among chemical treatments, the dilute sulfuric acid based pretreatment is most popular by means of enzymatic hydrolysis using biomasses such as cashew apple pulp and coffee pulp in India, which contains about 23–27% fermentable sugars on dry weight basis [144,145].

### 4.3. Biological pretreatment

In the biological pre-treatment process, the various microorganisms like brown rot, white rot and soft rot fungi may be used as degradation of the lignocellulosic complex to liberate cellulose. [16]. This pre-treatment also help in the degradation of lignin and hemicelluloses to produce amorphous cellulose [31,146] and white rot fungi give the impression to be the most effective microorganism. Brown rot help to attacks on cellulose, while white and soft rots attack both cellulose and lignin [146]. In most cases of biological pretreatment the rate of hydrolysis is very low while this method is safe and energy saving due to less mechanical support [16]. It needs no chemicals but low hydrolysis rates and low yields impede its implementation [33,147]. Zang et al. [148] reported that white rot fungi has been used as effective biological pre-treatment for bamboo culms at low temperature (25 °C). This biological pretreatment is cost effective and environment friendly process to release the sugars from the lignocellulosic matrix of sugarcane trash by using a number of microorganisms. Singh et al. [149] also reported that the reduction in the cellulose content by *Aspergillus terreus* was about 55.2%, while delignification was found to be about 92%. The biological process include myriad of microorganism. Since, these technologies such as physical and chemical, both of them require larger energy inputs to disrupt the lignin component that are more expensive, biological pretreatment is the best alternative technology.

## 5. Enzymatic hydrolysis

Enzyme hydrolysis is the critical step for bio-ethanol production where complex carbohydrates are converted to simple monomers. It requires less energy and mild environment conditions compared to acid hydrolysis [150]. In this process, cellulose enzyme is most important enzyme, which is naturally occurring in cellulolytic microbes e.g. *Clostridium*, *Cellulomonas*, *Thermonospora*, *Bacillus*, *Bacteriodes*, *Ruminococcus*, *Erwinia*, *Acetovibrio*, *Microbispora*, *Streptomyces* and other fungi such as *Trichoderma*, *Penicillium*, *Fusarium*, *Phanerochaete*, *Humicola*, *Schizophillum* sp. These enzymes have ability to convert the cellulose to glucose or galactose monomer. Neves et al. [151] reported that the optimum condition for cellulose is 40–50° temperature and 4–5 pH. Similarly, the optimum conditions for xylanase have also been reported

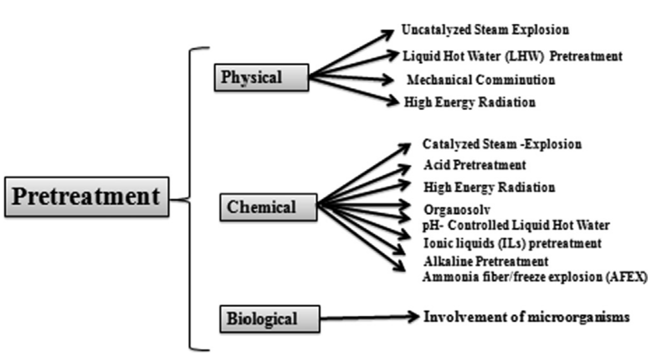


**Fig. 8.** Different process of pretreatment [142].

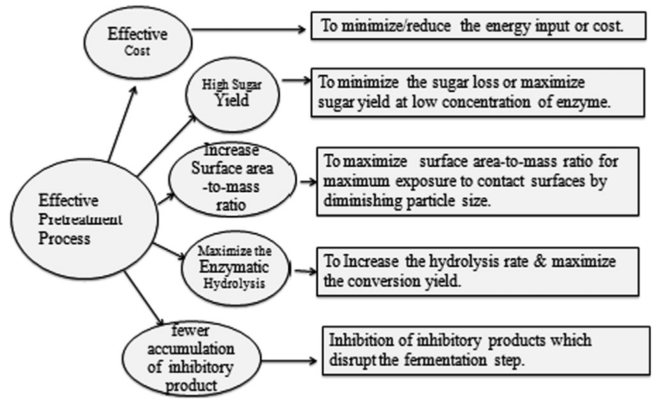


**Fig. 9.** Characteristics of an effective Pretreatment Process [13,14,133,128].

to be 50 °C temperature and pH 4–5 [152]. Consequently, enzymatic hydrolysis is beneficial because of its low toxicity, low utility cost and low corrosion compared to acid or alkaline hydrolysis [16]. Furthermore, no inhibitory by-product is formed by enzymatic hydrolysis [150]. The cellulase enzyme is highly substrate specific [29]. The cellulase and hemicellulase enzymes cleave the bonds of cellulose and hemicellulose respectively. Cellulose contains glucan and hemicellulose contains different sugar units such as mannan, xylan, glucan, galactan and arabinan. Cellulase enzymes are three types which involve endo and exoglucanase and β-glucosidases. Endoglucanase (endo 1,4-D glucanhydrolase or E.C. 3.2.1.4) attacks the low crystallinity regions of the cellulose fiber, exoglucanase (1,4-β-D glucan cellobiohydrolase or E.C. 3.2.1.91) removes the cellobiase units from the free chain ends and finally cellobiose units are hydrolyzed to glucose by β-glucosidase (E.C. 3.2.1.21) [47,153]. Hemicellulolytic enzymes are more complex and are a mixture of at least eight enzymes such as endo-1,4-β-D-xylanases, exo-1,4-β-D xylocuronidases, α-L-arabinofuranosidases, endo-1,4-β-D mannanases, β-mannosidases, acetyl xylan esterases, α-glucoronidases and α-galactosidases [41]. Cellulose is hydrolyzed to glucose whereas hemicellulose gives rise to several pentoses and hexoses.

### 5.1. Enzyme cellulase and their mode of action

The degradation of cellulosic biomass is accomplished by the most prominent form of associated enzymes i.e., cellulases (Fig. 11) [154]. The complex form of cellulase consist of Endoglucanases (1,4-β-D-glucanohydrolases), and Exoglucanases that also contains Cellodextrinases (1,4-β-D-glucan glucanohydrolases), Cellobiohydrolases (β-D-glucan cellobiohydrolases), and β-Glucosidases (β-glucoside glucohydrolases) [15]. On the other hand Lynd [155] classified cellulases into groups such as complex and non-complex cellulases. Many anaerobic bacteria are producing complexed form of cellulses for instance, *Clostridium thermocellum*. While aerobic fungi and bacteria producing non-complexed form of cellulases such as *Trichoderma reesei* [156]. Medve et al. [157], Saxena et al. [13], Lin et al. [156] reported that *T. reesei* secretes three types of extracellularly cellulolytic enzyme, together with five endoglucanases, two cellobiohydrolases and two β-glucosidases BGL. Whereas Duncan et al. [158] classified at least 92 species of *Trichoderma* most of which are uncharacterized, that signifying immense prospective for identifying novel cellulase-producing strains [118]. For ethanol production from cellulose chain firstly, there is need to break down of cellulose form fibrilated structure of cellulose chain which is embedded in plant cell wall which is made up of parralles unbranched D-glupyranose units linked by β-1,4 glycosidic bonds to form highly crystalline and organized microfibrils through extensive inter and intramolecular hydrogen

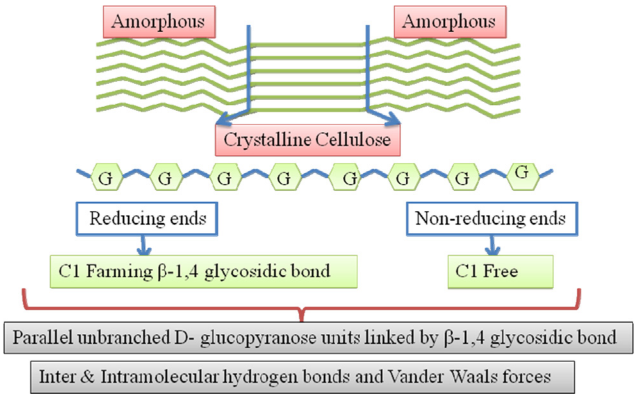


**Fig. 10.** Structure of amorphous and crystalline form of cellulose.

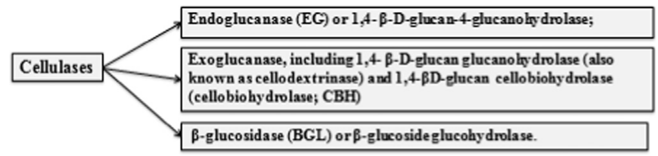


**Fig. 11.** Types of cellulase enzyme [154].

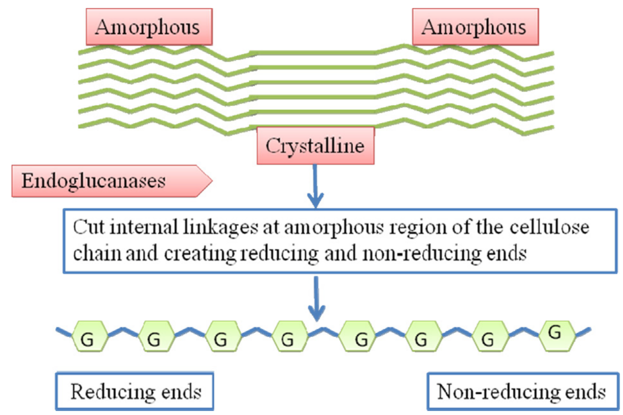


**Fig. 12.** Function of endoglucanases.

bonds and Van der Waals forces as shown in Fig. 15 [141,159–163]. Enzymatic hydrolysis requires a group of cellulase enzymes (Fig.11) [154]. The cellulose mutually consists of amorphous and crystalline form of cellulose (Fig. 10), of which crystalline form represents a regular arrangements of cellulose chain, which is very complicated to break down, while amorphous form (correspond to regions where this bonds are broken down and the ordered arrangement is lost) showing mishmash structure, which is rather easy to cut than crystalline form.

### 5.1.1. *Endoglucanases*

Firstly, the endoglucanases randomly incises at internal amorphous sites in the cellulose polysaccharide chain generating oligosaccharides of various lengths by inserting a water molecule in the 1,4-β bond (Fig. 12) or the enzymatic hydrolysis is initiated by endoglucanases that randomly carve internal linkages at amorphous regions of the cellulose fiber and creating new reducing and non-reducing ends that are susceptible to the action of cellobiohydrolases [131].

### 5.1.2. *Exoglucanases*

Exoglucanases also known as cellobiohydrolases, catalyze the successive hydrolysis of residues from the reducing and non-reducing ends of the cellulose, releasing cellobiose molecules as main product, which are hydrolyzed by β-glucosidases (Fig. 13). They account for 40% to 70% of the total component of the cellulase system, and are able to hydrolyze crystalline cellulose [131]. Consequently, the exoglucanases cut cellulose chain at its reducing and non-reducing ends and generates cellobiose (cellobiohydrolase) i.e., repeating unit of two glucose units.

### 5.1.3. *β-Glucosidase*

β-Glucosidase hydrolyzes soluble cellobiose and other cellodextrins to produce glucose (Fig. 14 in the aqueous phase in order to eliminate cellobiose inhibition [15,131]. Naturally, 90–95% of aerobic bacteria and fungi play a leading role in the degradation of cellulose and rest about 10% account for diverse anaerobic bacteria [118,164].

## 5.2. *Diversity of effective and efficient cellulolytic microorganisms (bacteria and fungi)*

Cellulose degrading microorganisms are known as cellulolytic microorganism. Wilson [165] acknowledged that most of microorganisms secret up to 50% of their protein during growth of cellulose or other biomass and have ability to degrade recalcitrant plant cell wall. Some wood feeding insects such as silver cricket, termite and beetle and Herbivorous mammals (cow and buffalo), goat, and cockroach have cellulolytic microorganisms within their gut and body. The rumen of mammalian animals, have natural cellulose-degrading system, contains various types of cellulose degrading microorganisms having capability to digest cellulosic biomass such as agriculture residues or organic fraction of the municipal solid wastes and aquatic plants [155,166–168]. Soil, the host of innumerable microbes mainly bacteria, plays significant function in decomposing cellulose-based materials [169]. Bacteria, Archaea, flagellates (formerly named Archaezoa) and yeasts and fungi too, have dense microbial gut activity for cellulose degradation [170]. These microorganisms possess enzymes to degrade cellulose component, which is the most abundant renewable source of energy on the earth [129,171], through diverse enzymatic activity known as cellulases [169,172,173]. A majority of microorganisms have been identified for cellulosic degradation biomass. The cellulolytic microorganisms such as thermophiles and mesophiles anaerobes and aerobes fungi and bacteria are strongly competent to hydrolyze highly crystalline insoluble cellulose comprehensively (Tables 12 and 13) [118,174,175]. Lamed and Bayer [176] reported that the thermophilic microorganisms are of particular interest because it has knack to produce thermostable cellulase under decidedly acidic and alkaline pH and above 90 °C temperature too. Mitchell [177] reported that, among these some microorganisms like *Clostridium* (cellulolytic bacterial group), a thermophilic anaerobe bacteria, help in the degradation of cellulosic plant biomass and has adaptable fermentable capabilities. Shaw [175] and Ueno et al. [178] reported another class of clostridia, a *Thermoanaerobacterium*, anaerobic hemicellulolytic bacteria that ferment pentose sugar into ethanol and hydrogen at elevated temperature [179] and they concluded that bacteria showed dominant lignocellolyitc microbial taxa among the microbial community.

## 6. Fermentation and distillation

Both fermentation and distillation is very vital steps for bio-ethanol production. Many microorganisms have been recognized for fermentation of sugars. However, the industrial utilization of lignocelluloses for bio-ethanol production is delayed due to lack of

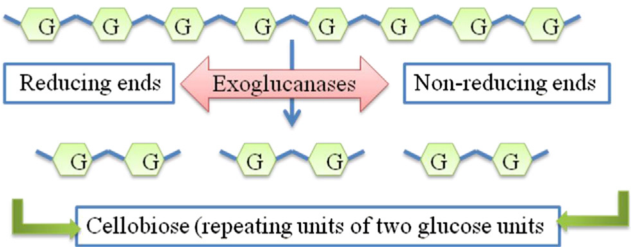


**Fig. 13.** Function of exoglucanases.

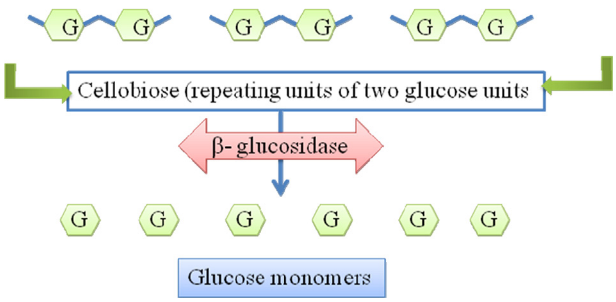


**Fig. 14.** Function of β-glucosidase.

ideal microorganisms, which can efficiently ferment both pentose and hexose sugars [28]. For a commercially viable ethanol production method, an effective microbe should have broad substrate utilization, high ethanol yield and productivity at high temperature. Therefore, genetically modified microbes are required to achieve complete utilization of the sugars in the hydrolysate and better production of ethanol. The processes generally used in fermentation of lignocellulosic hydrolysate are simultaneous saccharification and fermentation (SSF) and separate hydrolysis and fermentation (SHF). Conventionally or traditionally the SHF process has been used except SSF is superior for ethanol production since it can get better ethanol yields by removing end product inhibition and eliminate the need for separate reactors. This process is also cost effective although difference in optimum temperature conditions of enzyme for hydrolysis and fermentation poses some restrictions [16,18,147,151].

Wyman et al. [134] reported that robust *Saccharomyces* yeast [180], a common microorganism can produce around 90% of ethanol from glucose of theoretically yields or bacteria viz., (*E. coli*) can be used to produce ethanol from simple sugars [133]. Abbi et al. [181,182] explained that *S. cerevisiae* ferment only hexose sugar and it is unable to ferment pentose sugar and reported some microorganism, which is able to efficiently ferment pentose mainly xylose into ethanol are *P. stipitis*, *P. tannophilus* and *C. shehatae.* Similarly, Rubin [183] reported that among pentose ferment microorganisms *P. stipitis*, a yeast species, has natural ability to ferment pentose sugar. After enzymatic hydrolysis of cellulose by adding numerous cellulolytic microorganisms and their mutual enzymatic activity, it releases a surplus amount of glucose. Hence, to stop the reduction of formation or accumulation of glucose, fermentive microorganisms can be added to produce ethanol from glucose. This is known as simultaneous saccharification and fermentation (SSF). Tong et al. [133] explained the simultaneous saccharification and fermentation (SSF), most commonly used techniques, which is carried out by combining fermentation and enzyme hydrolysis in the similar step.

Except for SSF or SHF, the available alternatives are consolidated bioprocessing (CBP) and simultaneous saccharification and co-fermentation (SSCF) [184]. The means of CBP; cellulase production and biomass hydrolysis and ethanol fermentation are all together passed out in a single reactor [18]. This process is also

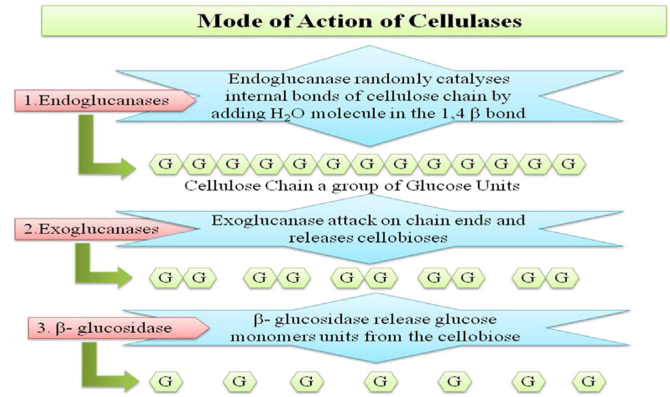


**Fig. 15.** Mode of action and function of cellulase [141,159-163].

known as direct microbial conversion (DMC). In this process, single or combined consortia of microorganisms are commonly used to ferment cellulose directly to ethanol. The application of CBP requires no resources investment for purchasing enzyme or its production [147,185]. Microbes such as *C. thermocellum* and some fungi including *Neurospora crassa*, *Fusarium oxysporum* and *Paecilomyces* sp. have ability for CBP. But, CBP is not an efficient process because of poor ethanol yields and long fermentation periods (3–12 days) [186]. In SSCF, the co-fermenting microorganisms require to be friendly in terms of operating pH and temperature [151]. A combination of *C. shehatae* and *S. cerevisiae* was reported as effective strains for the SSCF process [151]. Some indigenous or wild type microbes used in the fermentation are *S. cerevisiae*, *E. coli*, *Z. mobilis*, *P. tannophilus*, *C. shehatae*, *P. stipitis*, *C. brassicae*, *M. indicus* etc. [16,33–37]. Genetically modified microorganisms (GMMs) have been used to develop the different aspects of fermentation for higher yield of ethanol by better and wide substrate utilization to increased recovery rates. Some GMMs like *P. stipitis* BCC15191 [27], *P. stipitis* NRRLY-7124 [37], recombinant *E. coli* KO11 [187], *C. shehatae* NCL-3501 [182], *S. cerevisiae* ATCC 26603 [188] have been developed. The other microorganisms such as *K. marxianus*, *Candida lusitanieae* and *Z. mobilis*, *Clostridium* sp. and *Thermoanaerobacter* sp. have been also proposed for fermentation of sugar to convert ethanol [18,194].

## 7. Application of bio-ethanol as a bio-energy resource

Bio-energy, a carbon neutral technology is used to convert biomass into energy [127]. Ethanol is mostly used as fuel additives to cut down vehicles, which run on mixture of gasoline and up to 85% ethanol, are now available. Bio-energy encompasses three major domain of sustainable development i.e., economic, environment and social (Table 14) [12]. Bio-ethanol trims down Green house gases emission as well as air pollution, the global climate change and carbon dioxide upsurge [189]. Air pollution is due to combustion of fossil fuels and leading to emission of various GHGs (the main GHGs are $CO_2$, $N_2O$, $CH_4$, $SF_6$ and chlorofluorocarbons). Bio-fuel, particularly ethanol, reduces both world's burgeoning energy demand and GHG's emissions from fossil fuels. Similarly Galbe and Zacchi [190] stated that bio-ethanol, which is the world's most available renewable source, lessens the dependence of mankind as a transportation fuel on fossil fuel [130]. Bio-fuel includes solid, liquid and gas and the major bio-fuels encompass bio-ethanol, biodiesel, biogas, bio-methanol, bio-syngas ($CO+H_2$), bio-oil, bio-char, bio-hydrogen, Fischer–Tropsch liquids petroleum, and vegetable oil, out of which bio-ethanol and biodiesel are liquid transportation fuel, used as an additive source. Bio-ethanol is a

**Table 12**
List of bacterial diversity and their habitats.

| Bacterial diversity | | | | | |
|---|---|---|---|---|---|
| Aerobes (free, noncomplexed cellulases) | | | Anaerobes (complex or free, noncomplexed) | | |
| Species | Sources | Reference | Species | Sources | Reference |
| *Mesophilic ($\leq 50$ °C)* | | | *Mesophilic ($\leq 50$ °C)* | | |
| *Streptomyces reticuli* | Soil | [127] | *Fibrobacter succinogenes* | Rumen | [127,178] |
| *Sorangium cellulosum* | Soil | [127,178] | *Prevotella ruminicola* | Rumen | [176] |
| *Cellulomonas fimi* | Soil | [174] | *Ruminococcus albus* | Rumen | [118,174,175] |
| *Cellvibrio japonicus* | Soil | | *Ruminococcus flavefaciens* | Rumen | [176] |
| *Cytophaga hutchinsoni* | Soil comp | [127,178] | *Eubacterium cellulosolvens* | Rumen | |
| *Brevibacterium linens* | Comp | [127] | *Butyrivibrio fibrisolvens* | Bovin | [127] |
| | | | | Rumen | [127] |
| *Pseudomonas fluorescens, P. putida* | Soil sludge | | *Acetivibrio cellulolyticus* | Sewage | |
| | | [127,178] | | | [127,178] |
| *Bacillus brevis* | Termite gut | [127] | *Bacteroides cellulosolvens* | Sewage | |
| | | [127,178] | | | [176] |
| *Saccharophagus degradans* | Rot marsh grass | | *Clostridium cellulolyticum* | Comp | [127,178] |
| *Bacillus pumilis* | Rot biomass | [127] | *Clostridium josui* | Comp | [176] |
| | | | *Clostridium cellulovorans* | Woodfermenter | [176] |
| | | | *Clostridium papyrosolvens* | Mud (freshwater) | |
| | | | *Clostridium phytofermentans* | Soil | |
| *Thermophilic ($>50$ °C)* | | | *Thermoophilic ($>50$ °C)* | | |
| *Caldibacillus cellovorans* | Comp | [127] | *Anaerocellum thermophilum* | Hot spring | [176] |
| *Thermobifida fusca* | Comp | [118,174,175] | *Caldicellulosiruptor saccharolyticus* | Hot spring | [176] |
| *Cellulomonas flavigen* | Leaf litter | [127] | *Rhodothermus marinus* | Hot spring | [176] |
| | | | | | [176] |
| *Acidothermus cellulolyticus* | Hot spring | [127,178] | *Spirochaeta thermophila* | | [176] |
| | | | *Thermotoga neapolitana* | Hot spring | |
| | | | *Clostridium thermocellum* | Sewage, soil, manure | [127,178] |
| | | | *Clostridium stercorarium* | Comp | [176] |
| | | | *Thermotoga maritime* | Mud (marine) | [176] |
| *Psychrophilic/psychrotolerant($<20$ °C)* | | | *Psychrophilic/psychrotolerant($<20$ °C)* | | |
| *Pseudoaltermonas haloplanktis* | Antarctica | [127] | *Clostridium sp. PXYL1* | Cattle manure | [127] |

**Table 13**
List of Fungal diversity and their habitat.

| Fungal diversity | | | | | |
|---|---|---|---|---|---|
| Aerobes (free, noncomplexed cellulases) | | | Anaerobes (complex or free, noncomplexed) | | |
| Species | Sources | Reference | Species | Sources | Reference |
| *Mesophilic ($\leq 50$ °C)* | | | *Mesophilic($\leq 50$ °C)* | | |
| *Coprinus truncorum* | Soil comp | [118,174] | *Anaeromyces mucronatus* 543, *Caecomyces communis*, *Cyllamyces* | Rumen | [118] |
| *Trichocladium canadense* | Soil | | *aberensis*, *Neocallimastix frontalis* | | |
| *Trichoderma reesei* | Soil, rot canvas | [118,174,195] | | | [126] |
| | | | Neocallimastix patriciarum | Rumen | [127,178] |
| *Hypocrea jacorina* | Soil, rot canvas | [126] | *Orpinomyces joyonii* | Rumen | [126] |
| | | [176] | | | |
| *Penicillium chrysogenum*, *Aspergillus nidulans*, *A. niger* | Soil rot wood | [127,178] | *Piromyces equi 46 both* | Rumen | |
| | | | *Piromyces* E2 | Faces | |
| *Phanerochaete* | Comp | | | | |
| *chrysosporium* | | [127,178] | | | |
| *Agaricus bisporus* | Mush Comp | [127,178] | | | |
| *Thermophilic ($>50$ °C)* | | | *Thermoophilic ($>50$ °C)* | | |
| *Chaetomium* | Soil | [127,178] | Not available | | |
| *thermophilum,Thielavia terrestris*, *Paecilomyces thermophila* | | | | | |
| | Soil comp | [127,178] | | | |
| *Humicola grisea* | Soil comp | | | | |
| *Talaromyces emersonii* | Comp | [126] | | | |
| | | [126] | | | |
| *Psychrophilic/psychrotolerant ($<20$ °C)* | | | *Psychrophilic/psychrotolerant ($<20$ °C)* | | |
| *Cadophora malorum*, *Penicillium roquefortii* | Antarctica wood | [126] | Not available | | |

**Table 14**
Economical and environmental importance of bioenergy [12].

| Economic impacts | Environmental impacts | Energy security |
|---|---|---|
| Sustainability | Greenhouse gas reductions | Domestic targets |
| Fuel diversity | Reducing of air pollution | Supply reliability |
| Increased number of rural manufacturing jobs | Biodegradability | Reducing use of fossil fuels |
| Increased income taxes | Higher combustion efficiency | Ready availability |
| Increased investments in plant and equipment | Improved land and water use | Domestic distribution |
| Agricultural development | Carbon sequestration | Renewability |
| International | | |
| Reducing the dependency on imported petroleum | | |

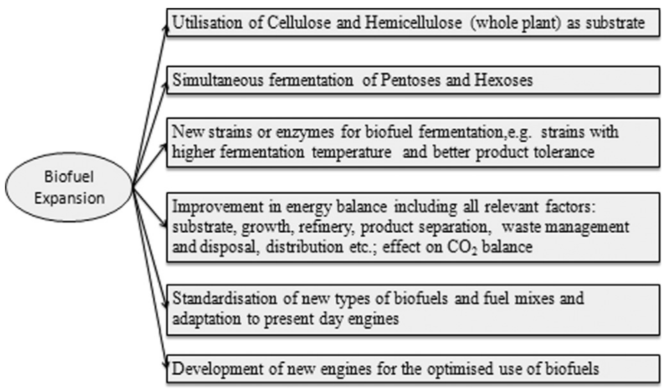


**Fig. 16.** Future biofuel expansion approach [62].

gasoline alternate, while biodiesel is a diesel alternate to reduce the GHGs emission when blended as an additive.

## 8. Research gaps and challenges

Bio-energy stores assets of technical information, which requires sustainable as well as carbon-neutral source of energy so as to balance the appropriate maintenance of food supply for securing the higher demand of energy and to reduce the environmental threat. Hence, it would be promising step to choose the energy based as well as agro-waste crops having high sugar level and high cellulose yield [191] and higher biomass yield; therefore it will trim down the rivalry with food production and nature preservation (Fig. 16) [62]. For efficient bio-fuel production, biological research will continuously desired to improve breeding of energy plants, enzymatic hydrolysis, specialized fermentation strains as well as waste treatment (Table 15) [191].

Due to the complex crystallinity of cellulose structure, cellulase enzyme is required to convert cellulose chain into simple sugar; however, it is an expensive process and takes long time for good result. The various pretreatment techniques are being adopted to unwind the cellulosic biomass such as physiochemical process, which are too much expensive, so proper pretreatment methods must be adopted to increase the concentration of fermentable sugar; thereby improving efficiency of entire process [16]. Hence, a progressively and promising research is needed to lessen the cost of enzymes [192].

Another hurdle in the selection of microorganism for an proficiently bio-fuel production is that only those microorganisms should be selected having both complexed and non-complexed form of cellulases or some genetically engineered microorganism are needed or super microorganisms or enzymes that can be used nowadays for rapidly saccharifying plant cell walls [118]. Also such robust microorganisms are required for fermentation of simple sugar into ethanol such as yeast (*S. cerevisiae*, *P. stipitis*), to *Z. mobilis*, to *E. coli*, which shows high productivity (that convert both $C_5$ and $C_6$ sugars at high rates), high tolerance to inhibitory compounds and can defend against the contamination of micro-organism from unnecessary microorganisms [13]. One of the best advantage of using cellulosic biomass to produce bio-fuels is that it can be produced anywhere in the world from home ground unprocessed material using presented farm machinery and grain circulation system [47].

## 9. Conclusion

Agro-residues biomass has been proposed to be one of the main renewable resources for cost-effectively attractive bio-ethanol production. The hypothetical ethanol yields from sugar and starch are superior compared to lignocelluloses agro-residues; however, these conventional sources are not enough for world-wide bio-ethanol production. In that aspect, agro-residues are renewable, less expensive and in large quantities available on earth crust. For the production of agro-residues, there is no need of separate land, water, and energy requirements and also they do not have food value additionally. The necessity of renewable and sustainable energy has commenced due to contraction/ shrinkage of non-renewable source of energy, which has resulted myriad of environmental as well as milieu problem the world is facing/ experiencing and hence drawing a prospective interest and attention towards bio-energy production from economically feasible biomass. It can be concluded that the cellulosic biomasses pay a key role to reduce the excessive consumption of non-renewable energy sources for energy production because of economical, less costly and environment friendly natural, renewable and sustainable energy sources. Thus, bio-ethanol from cellulosic biomasses will be promising entity to diminish various environmental and energy crisis predicaments. The processes of pretreatment, enzymatic hydrolysis, fermentation and distillation are the four major obstacles in bio-ethanol production and require to overcome by efficient technology. With reference to conversion technology the hindrances are biomass processing, proper and cost effective pretreatment technology to release cellulose and hemicellulose from their complex matrix with lignin. Under hydrolysis process, the challenge is to accomplish a competent process for depolymerization of cellulose and hemicelluloses to produce fermentable monomers with high concentration. Thus, the saccharification of cellulose chain needs an efficient and effective synergistic action of cellulose enzymes. Simultaneously the numerous efforts are being done to develop to efficient strain as well as to reduce the cost of production of enzymes for bio-ethanol production. Eventually fermentation process need fermentation of both pentose and hexose sugar co-fermentation, and the use of recombinant microbial strains. In the last, it may be supposed that to solve the technology bottlenecks of the conversion process, novel science and efficient technology are to be applied, so that bio-ethanol

**Table 15**
Potential challenges of bio-fuels [191].

| Feed stock | Technology | Policy |
|---|---|---|
| Collection network | Pretreatment | Land use change |
| Storage facilities | Enzyme production | Fund for research and development |
| Food-fuel competition | Efficiency improvement Technology cost | Pilot scale demonstration Commercial scale deployment |
| | Production of value added co-products | Policy for biofuels |
| | | Procurement of subcidies |
| | | On biofuels production |
| | | Tax credits on production |
| | | Utilization of biofuels |

production from agro-residues may be effectively developed and optimized in the near future.

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